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NANOCOMPOSITES RESEARCH FOR COMBAT RATION PACKAGING

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ABSTRACT

Nanocomposites of ethylene co-vinyl alcohol (EVOH) and montmorillonite layered silicates (MLS) were processed by extrusion methods to produce cast and blown films. Wide angle x-ray diffraction and transmission electron spectroscopy (TEM) showed that all the films had an intercalated morphology. TEM photographs of the cast films displayed random alignment of the nanoparticles while the blown films showed an ordered alignment of the nanoparticles. The samples were equilibrated at various humidities and the mechanical and barrier properties were evaluated. The blown film nanocomposites had better Young's modulus values, at higher humidity, than the cast film nanocomposites. The oxygen and moisture barrier properties improved the most in the cast nanocomposite films. The EVOH nanocomposite cast film had 57% improvement in oxygen barrier properties at 0% relative humidity in comparison to the pure EVOH cast film.

1. INTRODUCTION

The Meal, Ready-To-Eat (MRE) is key field survival food for the military. The MRE is used by the military to sustain individuals during operations that preclude organized food service facilities, but where re-supply is established or planned. Each soldier in combat potentially eats several MREs per day. The Army, Marine Corps, and the Air Force consume approximately 46.6 million meals in the field in an average year, generating approximately 14,117 tons per year or 0.66 lb of packaging waste per warrior per meal.

Currently, the MRE packaging contains foil-laminated films that provide the required three-year shelf life. Inherent problems such as flex cracking and pinholing exist with the use of these films especially when exposed to freezing temperatures. In addition, the use of foil-based structures limits the potential for recycling as well as the development of packaging systems for novel food processes currently being investigated, such as microwave and radio frequency sterilization. There is a need to develop recyclable and/or biodegradable MRE packaging, which offers high performance and sufficient barrier properties for the required shelf life of 3 years. Nanotechnology is being explored by the Army as a potential way to make new and improved MRE packaging.

Nanocomposites containing small amounts of nanoparticles (1-5%) have been shown to yield large improvements in barrier properties, as well as in physical properties such as tensile strength, tensile modulus and heat distortion temperature. (Brauer, 2000; Lucciarini et al., 2001; Marchant, D., 2002; Le Baron et al., 1999) A doubling of tensile modulus and strength without a sacrifice in impact resistance has been achieved for nylon 6/clay nanocomposites containing as little as 2 wt. % of clays. (Brauer, 2000, Leaversuch, 2001)

The nanoparticles commonly used in these nanocomposites are organically modified montmorillonite layered silicate (MLS), which consist of sheets arranged in a layered structure. MLSs are used due to their high cation exchange capacity and its high surface area, approximately 750 m^2/g and large aspect ratio (larger than 50) with a platelet thickness of 10 Å.

The closely stacked structure of the silicate layers and chemical incompatibility between the hydrophilic clay and hydrophobic polymer are two significant challenges that must be overcome when developing an exfoliated nanocomposite with improved properties. Organically modifying the MLS by replacing inorganic exchange cations with organic ions on the gallery surfaces has been shown to compatibilize the MLS and polymer, and also leads to an increased basel-spacing between the silicate layers due to the bulky organic ions. (LeBaron, 1999) Increased space between the platelets makes it easier for the polymer to penetrate the gallery and force the layers further apart to obtain exfoliation.

The large aspect ratio of the silicate layers has many benefits for several polymeric applications. The interface between the tremendous surface area of the MLS and the polymer matrix minimizes the chain mobility, creating a reinforcement effect. In addition, this interface facilitates stress transfer to the reinforcement phase, thus improving physical properties such as tensile strength and tensile modulus. (LeBaron et al,.1999; (Hunter et al. 2001) Because the MLSs contain so many individual particles in a relatively small amount of material, it takes low levels of loading (1-5%) to obtain a high concentration of constrained areas within the polymer (Ranade et al., 2002). More importantly for food packaging applications, these high aspect ratio nanolayers force gas and water molecules to follow a more tortuous path in the polymer matrix around the silicate layers. This results in much larger diffusion distances, thereby lowering permeability. (Brauer, 2000)

There are research and development programs at the Natick Soldier Center (NSC) focusing on the use of nanocomposites for MRE packaging. These programs encompass basic and applied research, primarily concentrating on melt processing of nanoparticles with commodity thermoplastics. Most of the studies begin with compounding trials using a mini-extruder and are then scaled up using laboratory size twin screw, single screw and co-extruders if potential is observed in the small-scale extrusion trials. Formulations are characterized by the techniques of x-ray diffraction and transmission electron microscopy (TEM) to evaluate the compatibility of the polymer and nanoparticle. This data also allows down-selection of several nanocomposite candidates. Blown or cast films are then produced while varying the following melt processing parameters: screw configuration, screw speed, take-off rate, feed rate, and temperatures. The mechanical, thermal, oxygen and water vapor barrier properties are analyzed and the barrier data is compared to the MRE specifications. Some of these nanocomposite systems have actually led to scale-up with pilot size extruders.

The polymers used in these research studies include: polyethylene, ethylene co-vinyl alcohol (EVOH), polyethylene terephthalate, polylactic acid and polyhydroyalkanoates. These polymers were all chosen based on their barrier properties and their potential as a food packaging. The focus of this paper is to present some research on the EVOH nanocomposites, including barrier and mechanical data as a function of moisture content. This is a continuation of an EVOH study that evaluated the thermal and mechanical properties of a variety of nanocomposites with MLS loadings of 1.5-6 percent. (Froio, 2004)

This study takes the 3% MLS loading nanocomposite and performs characterization of barrier and mechanical properties as a function of relative humidity. This EVOH system with different nanoparticles is a promising material for military rations.

EVOH, as shown in Figure 1, is a random copolymer of polyvinylalcohol (PVOH) and polyethylene and is, therefore, less hydrophilic than PVOH. Its properties depend on the ethylene vinyl alcohol composition ratio. EVOH with an ethylene content of 44% exhibits good mechanical properties. (Young's modulus = 2062 MPa; tensile strength = 58.87 MPa; elongation = 280%) and excellent oxygen barrier properties (oxygen transmission rate = 31.00 $cm^3 \cdot mil/(m^2 \cdot d)$). However, EVOH is sensitive to moisture which can render itself unsuitable for certain packaging applications. A number of EVOH grades, with varying levels of ethylene content, are available depending on required properties and processing method.

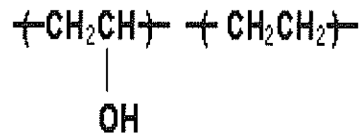


Figure 1. Structure of EVOH

For the military rations, some of the packaging undergoes sterilization at high temperature and pressure, which increases the oxygen permeability by moisture plasticization of the EVOH and causes irreversible changes in the EVOH structure. To retain its oxygen barrier in high humidity environments and after sterilization, EVOH is often co-extruded between two layers of a high moisture barrier material, such as polyethylene or polypropylene. Research on EVOH nanocomposites multilayer structures is now the target for the current research program.

2. EXPERIMENTAL

Commercially available EVOH (EVAL® E-105) was employed as the matrix polymer. E-105 has an ethylene copolymer ratio of 44-mol%. Southern Clay's organically modified MLS, Cloisite 25A, was compounded with EVOH. Cloisite 25A is modified with a quaternary ammonium salt as shown in Figure 2.

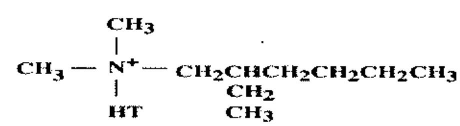


Figure 2. Structure of the organically modified montmorillonite.

Processing

Compounding was performed at Triton Systems, Inc. using a Zenix ZPT-30 30mm co-rotating twin screw extruder with a standard mid-shear configuration. The temperature profile of the nine zones increased from 170°C at the feed zone to 205°C at the die. E-105 was compounded with 3% 25A, at a screw speed of 300 rpm. Extruded strands were pelletized for secondary processing.

Blown and cast film samples were melt processed on a ThermoPrism co-rotating; completely intermeshing, twin-screw extruder with a 16 mm bore size and a L/D ratio of 24:1. The temperature profile increased from 195°C at the feed section to 200°C at the die, at a screw speed of 50 rpm.

Characterization

The morphology of the nanocomposite systems was first examined using wide-angle x-ray diffraction (WAXS) to determine *d*-spacing between the layered silicates. Samples were cryogenically milled using a SPEX CertiPrep 6750 Freezer/Mill, and observed using a Scintag XDS 2000 Diffractometer.

Transmission electron microscopy (TEM) was then used to confirm the degree of interaction between MLS and polymer matrix. Microtomed film and pellet samples were viewed under a JEOL 2010 FasTEM Transmission Electron Microscope at 200kV using various magnifications.

Many of the film samples were conditioned in humidity chambers at room temperature using saturated salt solutions. Samples were characterized at the following humidities: 0, 73, 87 and 93% for 45 days.

To examine the moisture content of the samples, a Mitsubishi Moisture Meter (Model CA-100) was used in conjunction with the VA-100 water vaporizer also from Mitsubishi. This unit applies the Karl Fischer coulometric titration method to measure moisture content through the reaction of iodine and sulfur dioxide with water. To analyze the sample, the water vaporizer was pre-heated to just below the melting temperature of the sample. Once the titration was complete, the unit displayed the moisture content of the sample in weight percentage and ppm levels. Several runs were carried out on the samples that equilibrated at a variety of relative humidities in order to accurately report the moisture content. Moisture absorption experiments were performed for each sample over a range of 50 days to determine the percent moisture absorption as a function of time for the samples.

Tensile properties, in the machine direction, were tested in accordance with ASTM D 882, using an Instron® 4400R. Samples were tested at a crosshead speed of 50.8 mm/minute using a 51kg tension load cell. Rectangular samples with a 50.8mm gauge length and 12.7mm width were used. Samples were dried at 70°C for 24 hours prior to testing.

Oxygen (OTR) and water transmission (WVTR) rates were established in accordance with ASTM D3985 and ASTM F1249 using the Mocon® Ox-tran 2/20 and Permatran at a temperature of 23°C, 37.8°C and 0 and 90% relative humidity.

3. RESULTS AND DISCUSSION

Morphology

WAXS and TEM are often referred to as complimentary techniques for studying morphology, each filling in gaps of information the other technique cannot obtain. (Morgan et al, 2003) WAXS was performed first to obtain a general understanding of how the MLS and polymer matrix interacted and to determine *d*-spacing. Figure 3 shows representative WAXS curves for the nanocomposite blown film and pure 25A.

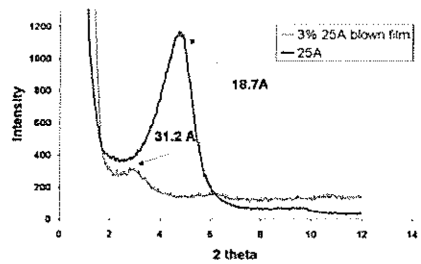
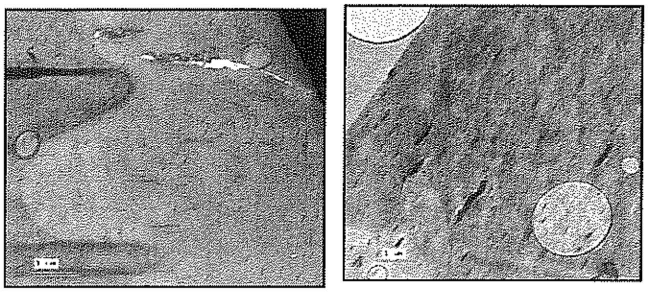


Figure 3. WAXS of the MLS and the blown film nanocomposite.

The peak pattern for the nanocomposite film shows a significant shift to the left, indicating interaction between the MLS and polymer. The increase in MLS *d*-spacing from 18.7 Å, prior to processing, to 31.2 Å after blown film processing, indicates that the extrusion process assisted in dispersion of the MLS. It is also important to point out that there was a slight increase in *d*-spacing from 29.0 Å to 31.2 Å between melt compounding and blown film, signifying additional MLS dispersion during blown film extrusion. As reported by Dennis et al., an average *d*-spacing between 20–30 Å indicates an intercalated system, therefore suggesting that this EVOH/MLS nanocomposite system, with a *d*-spacing of 31.2 Å, is highly intercalated. Dennis et al. also reports that full exfoliation does not occur until *d*-spacing has reached 80-100 Å. (Dennis, 2001)

The TEM images of both the cast and blown film compliment the WAXS results, and provide a better understanding of how 25A is dispersed within the polymer matrix. Figure 4a and 4b show low magnification TEM images of the cast and blown film, respectively. As show in Figure 4a, the cast film has MLS platelets in random directions throughout the EVOH matrix and undergoes uniaxial orientation. Figure 4b. reveals enhanced MLS alignment in the blown film, in comparison to the cast film. This is most likely due to the biaxial orientation the film is exposed to after exiting the die during blown film extrusion.



a) b)

Figure 4a and 4b. Cast film nanocomposite (a) and blown film nanocomposite (b) at 64,000x.

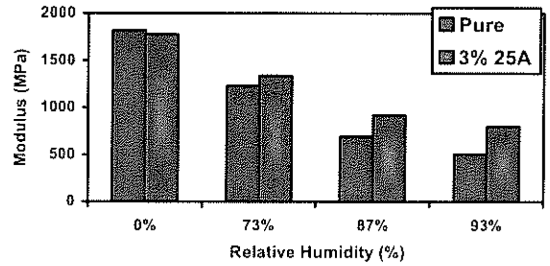


Figure 5a. Young's modulus of blown films. Pure EVOH and EVOH nanocomposite as a function of relative humidity.

Moisture Content

From the moisture content measurements at 93% humidity, the cast pure film contained 4.4% moisture while the nanocomposite had 6.4% moisture. The nanocomposite blown film samples at 93% relative humidity had approximately the same amount of moisture as the pure blow film, 4.3%. All films at 73% had approximately 3% moisture absorption. These experiments did not indicate that the nanocomposite had significantly different water content that may attribute to some of the data results for the barrier properties. Since the samples contain a small amount of the MLS, it is also assumed that solubility is not influencing the permeability properties. Further sorption isotherm experiments for the pure EVOH and the nanocomposites are ongoing to determine diffusion coefficients, which will aid in the understanding of the permeation of these films.

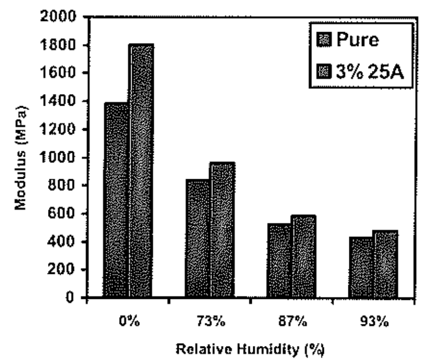


Figure 5b. Young's modulus of the cast films. Pure EVOH and EVOH nanocomposite as a function of relative humidity.

Mechanical

Examination of mechanical properties in the machine direction for the pure EVOH and nanocomposites blown and cast film as a function of moisture content are shown in Figure 5a and 5b respectively. For both pure and nanocomposite cast and blown films, the same trend occurs. The Young's modulus decreased as the relative humidity increased. For the blown films at relative high humidity, the nanocomposites had a higher Young's modulus than the pure E-105. (58% improvement) At dry conditions (0% humidity), there is no improvement in the modulus value for the nanocomposite. This is not expected since there is an intercalated morphology and the MLS stiff platelets normally increase the mechanical properties. The cast film has a 23% increase at 0% relative humidity but only a 11% improvement from the pure EVOH at the 93% relative humidity.

Barrier Data

Figure 6 illustrates the oxygen barrier data for the cast and blown films at 0% relative humidity. For the pure EVOH, the cast film is a much better oxygen barrier than the pure blown film. For the nanocomposites, there is a 57% improvement in barrier for the cast film, but a decrease of 14 % for the blown film samples compared to the pure EVOH controls.

In our previous study of EVOH and EVOH nanocomposites, the barrier properties were better for the biaxially oriented blown films than cast films. (Lucciarini, 2001) More experiments need to be performed for both cast and blown films to investigate why these differences are occurring. Segmental motion of the polymer chains may attribute to the barrier properties as well as the degree of orientation.

Permeability in nanocomposites can be influenced by the MLS orientation in the polymer matrix, the MLS sheet length as well as the state of aggregation and dispersion. An increased diffusion path length (tortuous path) is produced in the polymer/MLS systems by the overlapping of MLS platelets. Platelets must align parallel to the surface of the film to obtain the advantage of the tortuous path. If the platelet orientation is altered, then this can then alter the enhancement of barrier properties. Bissot (Bissot, 1989) has studied the effect of platelet orientation of oxygen barrier properties with EVOH and platelet-type fillers (mica, talc, and aluminum flake). Cast, blown and co-extruded films were processed and the barrier properties were dependent on this orientation.

Sharastri (Shrastri, 1989) studied the orientability and effect of orientation on high barrier films including pure EVOH. He was orienting in the solid state and actually was not successful at orienting the EVOH. However, for a vinylidene chloride/vinyl chloride (VDC) copolymer, there was 1.5 times higher permeability in the unoriented film with biaxial orientation than with a cast film. The crystallinity of the biaxially oriented film was actually less 24% versus the 33% of the extrusion cast film. Sharastri believes that microvoids can develop during the orientation and also the size of the crystallites may change, both factors influencing permeability.

Also, the decreased barrier effect of nanoparticles in the blown film, as compared to the improved barrier of the cast film, could be attributed to the effect of orientation on alignment of nanoparticles therefore reducing the projected area of the particles parallel to the surface.

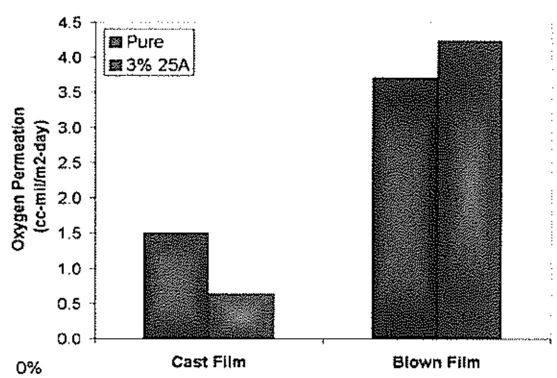


Figure 6. Oxygen permeation data at 0% relative humidity for cast and blown film EVOH and EVOH nanocomposites

Figure 7. Displays the oxygen barrier data at 90% relative humidity for the cast films. For the pure EVOH, there is an 11 times decrease in the barrier properties from the 90% relative humidity sample, and a 9 times decrease for the nanocomposite. The nanocomposite is 24% better than the pure EVOH.

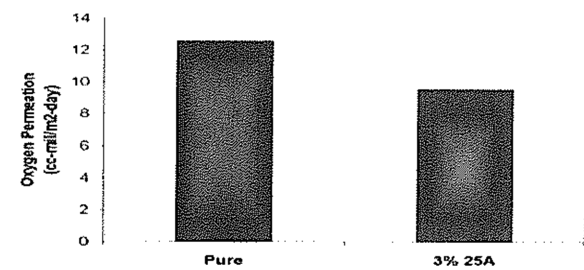


Figure 7. Oxygen permeation data for cast film samples at 90%RH and 23C.

Figure 8. Displays the water vapor permeation for the cast and blown films. There is the same trend for the cast and blown film that was viewed for oxygen. The blown film nanocomposite is a worse water vapor barrier than the pure EVOH by 34%, while the cast film nanocomposite shows a 29% improvement over the pure EVOH. This again can be attributed to the orientation in the EVOH and the nanoparticle in the matrix.

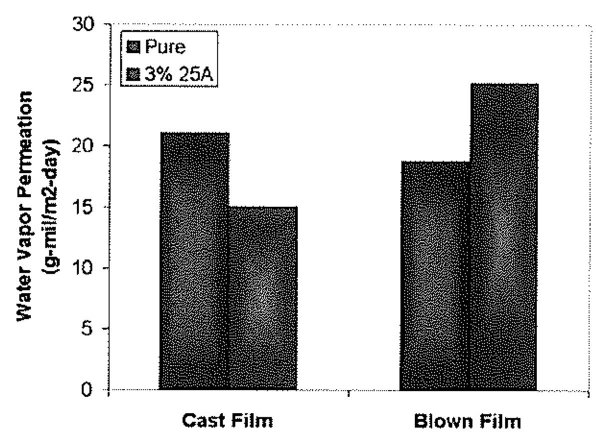


Figure 8. Water vapor transmission rate of cast vs blown film at 90% humidity and 37.8C.

CONCLUSION

EVOH nanocomposites of blown and cast films were processed and characterized to gain a better understanding of the EVOH/MLS system before multilayer extrusion films are prepared. EVOH barrier resins need to be utilized in co-extruded structures as a packaging film, but an understanding of the EVOH nanocomposites's mechanical and barrier properties as a function of moisture is crucial. The morphology of all the nanocomposites showed intercalated system and some dispersion. The mechanical properties of the films changed significantly with relative humidity. The barrier properties are also influenced by the amount of moisture in the sample. However, the orientation of the MLS platelets from the cast and blown film extrusion methods may be the underlining factor that is affecting the permeation properties.

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